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AD-E400 617

TECHNICAL REPORT ARLCD-TR-81008

STUDIES OF UNEXFOLIATED AND EXFOLIATED INTERCALATION GRAPHITE

W. L. GARRETT

J. SHARMA

J. PINTO

H. PRASK

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND  
LARGE CALIBER  
WEAPON SYSTEMS LABORATORY  
DOVER, NEW JERSEY

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report ARLCD-TR-81008 ✓	2. GOVT ACCESSION NO. <u>AD-A200 727</u>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) STUDIES OF UNEXFOLIATED AND EXFOLIATED INTERCALATION GRAPHITE		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) W.L. Garrett, J. Sharma, J. Pinto, and H. Prask		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS ARRADCOM, LCWSL Energetic Materials Division (DRDAR-LCE-P) Dover, NJ 07801		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS ARRADCOM, TSD STINFO Div (DRDAR-TSS) Dover, NJ 07801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS SA-01 6.1
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE May 1981
		13. NUMBER OF PAGES 16
		15. SECURITY CLASS. (of this report)  Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Smoke Obscurant Graphite Exfoliation Intercalation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The ongoing study of unexfoliated and exfoliated intercalation graphite is directed towards the understanding of its physical nature, to determine what changes take place when it is exfoliated into a low density solid, and to explore its potential as an obscurant. X-ray photoelectron spectroscopy (XPS) is used for studying the electronic levels; X-ray diffraction is used for crystallographic information, while optical reflectivity is measured to determine its spectral response. It has been found that even after exfoliation the material remains essentially graphite.		

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## INTRODUCTION

During the 1979 Chemical Systems Laboratory (CSL) Scientific Conference on Obscuration, attention was drawn to the fact that intercalated graphite of density approximately two can be exfoliated by sudden application of heat, to produce graphite whose density is about  $0.004 \text{ g/cm}^3$  which is only three times larger than that of air. Particles of 10 through  $35\mu$  size when dispersed in air will remain suspended for a long time and being composed of graphite, could be used as a battlefield obscurant. Graphite particles will be effective absorbers over a wide range of the electromagnetic spectrum from the ultraviolet to the microwave region embracing visible, infrared, and far infrared regions. This study reports on intercalated graphite before and after exfoliation. X-ray photoelectron spectroscopy has been applied to study the electronic states involved in the electrical conduction of the material. The XPS of the core levels gives information on chemical interaction in the material. X-ray diffraction has been used to study the changes in the lattice spacing both along the c-axis and in the plane of the hexagons. Optical reflectivity has been studied from 0.5 eV to 6.3 eV in the near visible region.

Most of the study has been performed on  $35\mu$  and  $120\mu$  unexfoliated and exfoliated graphite complex. Four specimens were provided by Dr. J. Maire of Le Carbone, Lorraine, Gennevillier, France. The complex is a proprietary commercial product of the Le Carbone Co., which is produced by the action of sulfuric and nitric acid; however, further details of the process are lacking. It appears that the exfoliation is achieved by the sudden application of heat to the complex.

In this laboratory, it has been possible to produce the exfoliated material from the complex by putting it into a furnace at  $1000^\circ\text{C}$ . Also, graphite intercalated with molecules of  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ , and  $\text{FeCl}_3$  obtained from Alpha products, Danvers, MA has been exfoliated in the same way. However, the density of the exfoliated specimen from Alpha products is not as low as that of the Le Carbone Co.

## EXPERIMENTAL RESULTS

### XPS Studies

X-ray photoelectron spectroscopy has been applied to study the valence and core levels of intercalated graphite both of the exfoliated specimen and of the complex before exfoliation. The valence band has been compared with that of diamond dust. Diamond being a large band gap insulator, has a density of states that reaches zero

at about 5 eV of binding energy (ref 1). In comparison to diamond, ordinary graphite shows the valence band extending to zero of the binding energy scale (fig. 1) although a well pronounced Fermi level, as exhibited by a metal, is not evident. All intercalated complexes showed increased density of state in the conduction band (figs. 1,2) due to the effect of intercalation. The  $\text{AlCl}_3$  and  $\text{AlBr}_3$  intercalates showed prominent structure in the valence band with peaks at 6 eV and 8 eV. These sharp peaks are direct contributions of the 3p and 4p levels of chlorine and bromine, respectively, and these levels are likely to be localized since the specimen had only 1 to 4% atomic concentration of the halogens. Exfoliation caused the valence band spectrum to become somewhat fuzzy so that the structure was reduced, but the extension to zero binding energy was not affected. The core levels of carbon showed no large shift due to intercalation or exfoliation.

Elemental analysis carried out with XPS techniques showed that in the  $120\mu$  specimen the atomic ratio of sulfur to carbon is about 3:100, while that in  $35\mu$  is 6:100. After exfoliation the ratio drops in both specimens by a factor of ten, which means that during heating most of the sulfur escapes from the specimen with some oxidized sulfur remaining. From the XPS study it can be concluded that exfoliation does not cause any reduction of electrical conduction. Therefore, exfoliated graphite should be a good obscurant over a large part of the spectrum.

#### X-ray Diffraction

In the X-ray diffraction work, the peak positions, peak shapes, and small angle scattering of Le Carbone intercalated graphite, both unexfoliated and exfoliated, have been studied and compared with pure Asbury graphite. From overall comparisons of diffraction patterns with Asbury graphite, it appears that the intercalation compounds possess an essentially undisturbed graphite structure, and that the intercalated molecules interact very weakly with the carbon lattice and fit easily into the open structure of graphite. A slight (0.3%) contraction along the c-axis has been observed. Usually expansion is expected (ref 2). The reported contraction disappears in the exfoliated specimen. No such contraction or expansion within experimental uncertainty was observed in the intercalated graphite in the plane perpendicular to the c-axis. Very definite low-angle scattering ( $2\theta < 3^\circ$ ) is shown by the exfoliated sample. This most probable arises from the porosity associated with the expansion.

Because of the tendency of the flakes to orient when packed in the plate-geometry X-ray sample holder, neutron diffraction measure-

ments were also performed. Three samples were studied: 35 $\mu$  complex, 35 $\mu$  exfoliated, and Asbury graphite. The results are in agreement with the X-ray diffraction measurements; however, a few additional features were revealed. High-angle side asymmetry observed with X-rays for the (002) reflection in all samples is apparently an instrumental effect. With neutrons, only the complex shows asymmetry, and this disappears after exfoliation. Furthermore, the asymmetry is of a complicated nature, consistent neither with simple strain nor crystallite-size effects. The (002) asymmetry suggests a nonuniform sample, part of which exhibits a slightly increased c-axis spacing, while the remainder is still normal graphite. In contrast to this, the (004) d-spacing for the complex shows a slight contraction - consistent with the X-ray results.

No new peaks or any significant changes in relative (00 $l$ ) intensity (neutron data) were observed so that definite intercalation stages do not seem to be present.

#### Optical Reflectivity

The optical reflectivity of the unexfoliated and exfoliated graphite was compared with that of ordinary graphite in the range between 0.5 eV to 6.3 eV (ref 3). No difference was observed.

#### Electron Microscopy

Scanning electron micrographs were taken of both the complex as obtained from Le Carbone and the complex after exfoliation in this laboratory. Photographs 321 and 323 (fig. 2) show particles of the complex at low (X 260) and high (X 1500) magnification. Particle sizes average about 50 $\mu$  and the layered structure of graphite is clearly evident. Photographs 202 and 203 (fig. 3) show particles after exfoliation at low (X 150) and high magnification (X 1400). The graphite layers are now expanded into a cell-like pattern which explains the low density. Additional photographs indicate a cell wall thickness of about 0.1 $\mu$  or less. Small spheres of graphite having a 0.1 $\mu$  wall thickness and a density of 0.004 g/cm<sup>3</sup> would have a radius of about 10 $\mu$ . Observed cell spacings are not at all uniform but are distributed over the range of 1 to 10 $\mu$ . Additional improvements in the method of preparing the exfoliated material that would either reduce the cell wall thickness or produce a lower density of cells would result in a material whose density would approach more nearly that of air.



## CONCLUSIONS

The present study leads to the following conclusions:

1. C-axis spacing shows slight decrease rather than increase in the Le Carbone specimen.
2. Exfoliation does not adversely affect the electronic density of states near the Fermi level. Thus, the exfoliated graphite is likely to be as good an obscurant as graphite.

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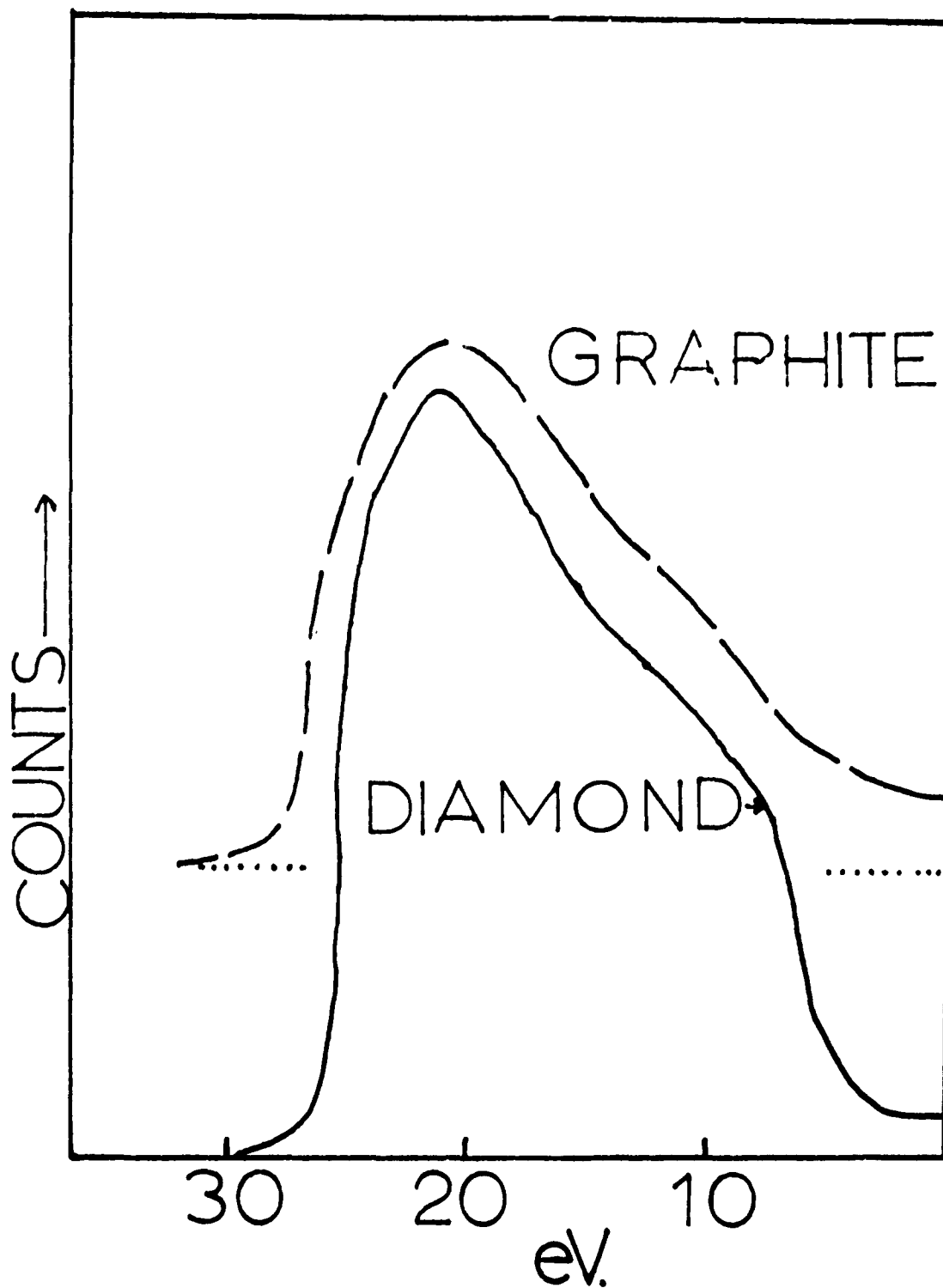


Figure 1. XPS valence band spectrum of diamond and graphite showing extension of occupied density of states in graphite beyond that of diamond



Figure 2. SEM photographs at different magnifications of the unexfoliated complex an obtained from La Carbon Co.



Figure 3. SEM photographs of the complex after exfoliation at 1000°C

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